

ON THE THEORY OF CRYSTAL STABILITY AND ELASTIC CONSTANTS OF
SIMPLE IONIC SOLIDS

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PAR

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Influence of Short-Range Three-Ion Interactions on Polymorphism and Elastic Constants of Simple Solids. I. Alkali Halide Crystals

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A theoretical analysis is made of crystal stability and of low-temperature deviations from the Cauchy relations between elastic constants of ionic crystals with AX composition and with cubic or hexagonal structure. The Born-Mayer model is used as a basis, extended to take into account short-range three-ion interactions of exchange type. These interactions are evaluated in first and second orders of perturbation theory, adopting a Gaussian effective-electron approximation. In the stability analysis, four different crystal structures ($B1$, $B2$, $B3$, and $B4$) are compared for each compound. In this paper, the results are reported for alkali halide crystals. Good agreement with experimental results is found. A following paper will deal with solid ionic compounds whose cations possess a complete outer d shell of electrons.

1. INTRODUCTION

IONIC solids of high symmetry and simple composition have long been the subject of a great many experimental and theoretical studies. Among the theories proposed to explain the properties of these solids, the so-called Born-Mayer model has been very successful in correlating macroscopic properties with interionic potentials. As is well known, the interionic potential in this model is a pairwise additive consisting of Coulomb interactions between the net ionic charges and of pair (overlap) repulsions between the (closed) electron shells on neighboring ions. These two components already stabilize a given structure for the solid, and in most cases it is unnecessary to consider additional terms in the potential, as, for example, the van der Waals long-range attractions. Further, if the symmetry of the unstrained crystal is sufficiently high, then polarization energy need not be taken into account.

The Born-Mayer model has been applied with particular success to alkali halide crystals. These solids are of high symmetry, exhibiting $B1$ (sodium chloride) or $B2$ (cesium chloride) structure; in $B1$ the two sublattices (cations on one, anions on the other lattice) are face-centered cubic, whereas, in $B2$ they are simple cubic. The coordination numbers are six for $B1$ and eight for $B2$. Only the heavy cesium halides possess $B2$ symmetry; all other alkali halides crystallize, at normal temperature and pressure, in $B1$. Transitions under pressure from $B1$ to $B2$ have been observed for many of the alkali halides.¹

In this paper, we will analyze two types of disagreement which have long been known to exist between the Born-Mayer model and experimental results regarding alkali halide crystals. First, the model predicts $B1$ as more stable than $B2$, at normal temperature and pressure, for all alkali halides; the difference in lattice energy is of the order of a few kcal/mole, i.e., a few percent of the crystal energy. For salts with $B1$ symmetry, the

calculated pressures of the transition to $B2$ are considerably higher than the experimental values. This result implies² that the Born-Mayer model overestimates the stability of $B1$ relative to $B2$.

The second disagreement concerns elastic constants. In view of the cubic symmetry of $B1$ and $B2$, there are only three independent elastic constants,³ namely, c_{11} , $c_{13}(=c_{12})$, and $c_{44}(=c_{66})$. If the interionic potential is pairwise additive and if zero-point and thermal energies can be neglected, then it is easily demonstrated that theoretically $c_{13}=c_{44}$ (a Cauchy relation). Recently, measurements at liquid-helium temperatures have become available for many alkali halides⁴; they show that generally $c_{13}\neq c_{44}$. The experimental values for $c_{13}-c_{44}$ are of either sign, although those with negative sign are more numerous.

Regarding the Cauchy relation $c_{13}-c_{44}$, the discrepancy must be ascribed to a deviation from pairwise additivity of the crystal free energy. At very low temperatures, only zero-point and static lattice energies need be considered. The contribution to $c_{13}-c_{44}$ by zero-point vibrations was analyzed by Leibfried⁵ and by Leibfried and Hahn⁶ in the quasi-harmonic approximation. The resulting values for $c_{13}-c_{44}$ are negative and too small to play a role for all but the lightest solids.

Consequently, the nonadditive component must be part of the static lattice energy, i.e., of the sum of interactions between all the ions in the solid. Herpin⁷ (see also Lothe⁸) pointed out that a contribution to the difference $c_{13}-c_{44}$ arises from polarization effects. In the unstrained crystal the polarization energy is very small in view of the high symmetry of the structure, consequently, polarization effects play no role for stability. On the other hand, the quadrupole component of the (three-ion) polarization energy of a strained (cubic)

² For an excellent review, see M. P. Tosi, *Solid State Phys.* **16**, 1 (1964).

³ H. B. Huntington, *Solid State Phys.* **7**, 213 (1958).

⁴ J. T. Lewis, A. Lehoczy, and C. V. Briscoe, *Phys. Rev.* **161**, 877 (1967), where additional references may be found.

⁵ G. Leibfried, *Handbook of Physics* (Julius Springer-Verlag, Berlin, 1955), Vol. VII, part 1, p. 104.

⁶ G. Leibfried and H. Hahn, *Z. Physik* **150**, 497 (1958).

⁷ A. Herpin, *J. Phys. Radium* **14**, 611 (1953).

⁸ J. Lothe, *Arch. Math. Naturvidenskab.* **55**, 82 (1959).

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¹ For recent compilations on transitions see C. E. Weir and G. J. Piermarini, *J. Res. Natl. Bur. Std.* **68A**, 105 (1964); W. Klement and A. Jayaraman, *Progr. Solid State Chem.* **3**, 289 (1967).

crystal yields a contribution to the difference $c_{13}-c_{44}$ which is always positive and not negligibly small. This effect varies as the inverse sixth power of the distance between the ions, implying that it is largely caused by the near neighbors of a central polarizable ion. At such small distances, the classical model used for the evaluation of polarization energy is, however, of doubtful validity.

A quantum-mechanical, *a priori*, calculation of the total energy for alkali halide crystals was first carried out by Löwdin⁹ on the basis of the Heitler-London approximation. The nonadditive part of the crystal energy has a leading three-ion component which can in essence be interpreted as an interaction between an "exchange charge" associated with a pair of overlapping ions and the Coulomb field of all the other ions. This main component is proportional to the Madelung constant of the lattice and large if cation and anion are of considerably different size. As the Madelung constants for the B1 and B2 lattices differ by only 1%, this three-ion energy has little effect with regard to B1-B2 relative stability. The results for $c_{13}-c_{44}$ are found to be of negative sign and of the correct order of magnitude for the salts considered (see also Lundqvist¹⁰ and Lothe⁸). Recent recalculations with improved free-ion wave function for lithium fluoride,¹¹ sodium fluoride,¹² and sodium chloride¹³ gave largely the same results as those obtained originally by Löwdin. Results for salts with positive experimental low-temperature values of $c_{13}-c_{44}$ (e.g., rubidium chloride) have so far not been obtained.

In terms of perturbation theory, the Heitler-London treatment corresponds to a first-order approximation. An extension of Löwdin's analysis to second order is necessary before an accurate comparison can be made. Such an extension, however, is prohibitively complicated for all but the simplest compounds on an *a priori* basis.

A model calculation based on Löwdin's theory, involving (point) exchange charges and their interactions with the Coulomb field of the ions and with each other, was undertaken by Dick.¹⁴ The contributions to $c_{13}-c_{44}$ are generally not in satisfactory agreement with the experimental values (for a comparison, see also Ref. 4).

The many-ion contributions to the crystal energy discussed so far pertain essentially to *long-range* interactions in the solid. In previous publications, we have analyzed the influence of *short-range* three-ion forces of exchange type on crystal stability for several classes of ionic solids.¹⁵⁻¹⁷ We assumed, as in the Born-Mayer

model, that the principal interactions result from overlap between the closed electron shells of neighboring ions and from the net ionic charges (Madelung energy). As an extension of the Born-Mayer model we considered also overlap (exchange) interactions between three ions simultaneously; these interactions were evaluated in first and second orders of perturbation theory using effective-electron wave functions of Gaussian form. It was shown that the observed B1-B2 polymorphism for alkali halide crystals can be explained on this basis and that detailed stability criteria can be formulated for several other classes of ionic solids of composition AX or AX_2 .

As a further implication of the non-Coulombic exchange, three-ion interactions we will in this paper consider their contribution to the difference $c_{13}-c_{44}$ between elastic constants of alkali halide crystals. The basis of the following analysis, is therefore, an interionic potential of the Born-Mayer type, extended to take into account short-range three-ion interactions. The main features of the effective-electron Gaussian model, to be used in the analysis, are summarized in Sec. 2.

2. THREE-ION INTERACTIONS IN EFFECTIVE-ELECTRON GAUSSIAN APPROXIMATION

Following are the main elements of the model to be used for the evaluation of the non-Coulombic part of the crystal energy and its contribution to the elastic constants. A more detailed description has been given in earlier papers.¹⁵⁻¹⁷ We start from complete ionicity and closed electron shells in zeroth order of perturbation theory, i.e., cation and anion have net charges of magnitude unity and thus are isoelectronic with rare-gas atoms. The zeroth-order wave function $\Psi^{(0)}$ for any triplet of ions is written formally as a Slater determinant of ionic wave functions which are of the correct symmetry with respect to intraionic exchange of electrons; the different components of the determinant describe states of different interionic exchange of electron pairs.

We follow a perturbation procedure¹⁸ in which the different orders are defined in terms of powers of a smallness parameter λ , as in Schrödinger perturbation theory without exchange. This implies a redefinition of the unperturbed Hamiltonian H_0 and the perturbation H' ; for the special case of two-hydrogen atoms (electrons labelled 1 and 2, nuclei a and b), these definitions are

$$\begin{aligned} H_0 &= H_0(1,2)\Lambda_{12} + H_0(2,1)\Lambda_{21}, \\ H' &= H'(1,2)\Lambda_{12} + H'(2,1)\Lambda_{21}, \end{aligned} \quad (1)$$

where Λ_{12} and Λ_{21} are linear operators which project from the permutation-symmetrized wave functions to

see also L. Jansen and E. Lombardi, Chem. Phys. Letters 1 33 (1967).

¹⁶ E. Lombardi and L. Jansen, Phys. Rev. 140, A275 (1965).

¹⁷ E. Lombardi and L. Jansen, Phys. Rev. 151, 694 (1966).

¹⁸ L. Jansen, Phys. Rev. 162, 63 (1967); L. Jansen and E. Lombardi, Chem. Phys. Letters 1, 417 (1967).

⁹ P. O. Löwdin, *A Theoretical Investigation into Some Properties of Ionic Crystals* (Almqvist & Wiksells boktryckeri AB, Uppsala, 1948).

¹⁰ S. O. Lundqvist, Arkiv Fysik 6, 25 (1952).

¹¹ K. Mansikka, J. Torsti, G. Petterson, J. Vallin, and J. L. Calais, Ann. Univ. Turku, Ser. A, I, 104 (1967).

¹² J. Vallin, G. Petterson, J. L. Calais, and K. Mansikka, Arkiv Fysik 34, 199 (1967); G. Petterson, J. Vallin, J. L. Calais, and K. Mansikka, *ibid.* 37, 267 (1968).

¹³ G. Petterson, J. Vallin, J. L. Calais, and K. Mansikka, Arkiv Fysik 34, 371 (1967).

¹⁴ B. G. Dick, Phys. Rev. 129, 1583 (1963).

¹⁵ E. Lombardi and L. Jansen, Phys. Rev. 136, A1011 (1964);

the associated simple-product functions. The symbol (1,2) denotes that electron 1 is associated with nucleus a , electron 2 with nucleus b , whereas, in the symbol (2,1) the association is just the reverse. The components H_0 and H' of (1) are separately permutation invariant, but they are not separately Hermitian. In view of their invariance under permutations, any linear combination $H_0 + \lambda H'$ is again invariant. This implies that the usual Schrödinger type of perturbation formalism can be developed.¹⁸

The first-order energy in this formalism is

$$E_1 = \langle \Psi^{(0)} | H' \Psi^{(0)} \rangle + C_1, \quad (2)$$

and the second-order energy

$$E_2 = -\epsilon^{-1} [\langle \Psi^{(0)} | H'^2 \Psi^{(0)} \rangle - \langle \Psi^{(0)} | H' \Psi^{(0)} \rangle^2] + C_2, \quad (3)$$

where ϵ is the Unsöld average energy. C_1 and C_2 are correction terms which are neglected in evaluating relative three-ion interactions for a triplet¹⁸ (relative to pair energies). The expressions (2) and (3) are of the same form as those in perturbation theory without exchange, except for the occurrence of C_1 and C_2 .

It is now assumed that for the evaluation of relative three-ion interactions we may restrict ourselves in first and second orders to single-exchange contributions, i.e., not more than one pair of electrons is exchanged between any two ions. On this basis, the first- and second-order perturbation energies can be written as sums of terms, each term involving the exchange of not more than one pair of electrons between different ions (summed over all electrons). We replace the perturbation expressions for each triplet of ions by exchange interactions between three "effective" electrons with parallel spins, one electron per ion.¹⁹ The three effective electrons for a triplet abc are labelled 1, 2, and 3 and the effective free-ion wave functions are denoted by ϕ_a , ϕ_b , and ϕ_c . The zeroth-order wave function $\Psi^{(0)}(abc)$ is then written as

$$\Psi^{(0)}(abc) = N \det[\phi_a(1)\phi_b(2)\phi_c(3)], \quad (4)$$

where

$$N = [3!(1 - \Delta_{abc}^2)]^{-1/2}$$

is the normalization constant, Δ_{abc} is a total overlap integral defined by

$$\Delta_{abc}^2 = \Delta_{ab}^2 + \Delta_{ac}^2 + \Delta_{bc}^2 - 2\Delta_{ab}\Delta_{ac}\Delta_{bc},$$

in terms of the overlap integrals Δ_{ab} , etc., for the three pairs of ions. The perturbation Hamiltonian H_{abc}' for the triplet can be written as

$$H_{abc}' = H_{ab}' + H_{ac}' + H_{bc}',$$

in terms of the perturbations between the three pairs. The effective wave function (4) will be used only to evaluate relative three-ion interactions. We call the approximation (4) the effective-electron approximation.

¹⁹ We recall that the perturbation energies refer to the non-Coulombic part of the crystal energy only, i.e., the ions may be taken as electrically neutral.

Denote the first-order energy by $E_1(abc)$, the total first-order pair energy by $E_1^{(0)}(abc) = E_1^{(0)}(ab) + E_1^{(0)}(ac) + E_1^{(0)}(bc)$. In second order, the corresponding quantities are $E_2(abc)$ and $E_2^{(0)}(abc) = E_2^{(0)}(ab) + E_2^{(0)}(ac) + E_2^{(0)}(bc)$, respectively. The three-ion energies for the triplet (abc) are then

$$\Delta E_1(abc) = E_1(abc) - E_1^{(0)}(abc)$$

and

$$\Delta E_2(abc) = E_2(abc) - E_2^{(0)}(abc).$$

Finally, we form the relative three-ion interactions (omitting the triplet label)

$$\Delta E_1/E_1^{(0)} = (E_1 - E_1^{(0)})/E_1^{(0)}$$

and

$$\Delta E_2/E_2^{(0)} = (E_2 - E_2^{(0)})/E_2^{(0)},$$

for each triplet of ions of the crystal. The reasons for evaluating relative, rather than absolute, three-ion energies are that these may be expected to show a similar behavior for different alkali halides and that relative quantities are generally less sensitive to the properties of a particular model than are the absolute energies. In addition, we suppose that the three-ion energies are only relatively small corrections to the pair contributions. In this case, the Unsöld average energy in E_2 may be identified with the corresponding quantity in the second-order pair energy $E_2^{(0)}$. This means that, in calculating the relative second-order three-ion energy $\Delta E_2/E_2^{(0)}$, the Unsöld energies in numerator and denominator cancel in good approximation.

The free-ion wave functions ϕ_a of Eq. (4) are determined, starting from the ϕ functions of the corresponding isoelectronic rare-gas atoms, following a procedure outlined earlier.¹⁵ It appears possible to choose for ϕ a Gaussian function

$$\phi(r) = (\beta/\pi^{1/2})^{3/2} e^{-\beta^2 r^2/2}, \quad (5)$$

where r is the distance from the effective electron to its nucleus and β is a characteristic parameter.

Each alkali halide is characterized by two Gaussian parameters, β (for the larger ion) and β' (for the smaller ion), i.e., $\beta' \geq \beta$. We also introduce the dimensionless parameter $\gamma = (\beta'/\beta)^2 \geq 1$. The first- and second-order energies can now be evaluated for each triplet (abc) . The first-order integrals are easy to compute; those of second order are determined following methods developed by Zimering²⁰ (for arbitrary γ values) and Roberts²¹ (special case of $\gamma = 1$).

The results can be described as follows.^{15,22} Consider a central ion a and two ions b, c at the same distance from it. If the ions are of the same kind (cations or anions), then the following equality holds to a good approximation:

$$\Delta E_1/E_1^{(0)} = \Delta E_2/E_2^{(0)}, \quad (6)$$

²⁰ S. Zimering, J. Math. Phys. 8, 1266 (1967).

²¹ P. J. Roberts, Proc. Phys. Soc. (London) 89, 67 (1966).

²² L. Jansen and E. Lombardi, Discussions Faraday Soc. 40, 78 (1965).

for all values of the opening θ of the triangle at the central ion. The relative three-ion energy amounts to about -0.2 at $\theta=60^\circ$ (equilateral triangle), increases rapidly and practically linearly with increasing θ , becomes positive between $\theta=90^\circ$ and 120° , and then flattens out. If the ions of the triplet are of different kinds (a central cation and two anions, or the converse) and of considerably different size ($\gamma \gg 1$), then we must consider only the three-ion interactions between the larger like ions and (6) holds again. Nonisosceles-triplet configurations contribute relatively little to the three-ion energy.¹⁵ To determine the total three-ion energy of the crystal we may, therefore, start from a central ion and consider only triplets of which the two remaining ions are in the same shell around the central one. Since three-ion interactions are of exchange type, only a few shells around a central ion must be considered.

Finally, let us denote the sum of first- and second-order energies for a triplet of ions by $\Delta E = \Delta E_1 + \Delta E_2$, the sum of its first- and second-order pair energies by $E^{(0)} = E_1^{(0)} + E_2^{(0)}$. The total relative three-ion energy $\Delta E/E^{(0)}$ for the triplet is, in view of (6),

$$\Delta E/E^{(0)} = \Delta E_1/E_1^{(0)} = \Delta E_2/E_2^{(0)}. \quad (7)$$

Expression (7) is the basic equation for the evaluation of the non-Coulombic three-ion component of the crystal energy.

3. STATIC LATTICE ENERGY

The Born-Mayer model of ionic solids is now extended by including short-range three-ion interactions while preserving the basic validity of the Born-Mayer potential as an "effective" potential. The static lattice energy has the following components. First, the Madelung energy E_M , i.e., the Coulomb interaction, per mole, between the net ionic charges, given by $E_M = -Ae^2/R_0$, where A is the Madelung constant and R_0 is the nearest-neighbor distance in the lattice. Further, the non-Coulombic (overlap) repulsion, for a pair (ab) of ions, is denoted by $E_{\text{rep}}^{(0)}(ab)$; this quantity is equal to the total non-Coulombic pair energy minus the nonexchange van der Waals attraction. Finally, the (exchange) many-ion component ΔE_{st} of the lattice energy is to be evaluated in first and second orders of perturbation theory. The leading term of ΔE_{st} is assumed to be given by three-ion interactions, i.e., clusters of more than three ions contribute relatively little to the many-ion energy. We can then write

$$\Delta E_{\text{st}} = \sum_{a < b < c} \Delta E(abc),$$

as a sum over all triplets (abc) of the lattice. The static lattice energy now assumes the form

$$E_{\text{st}} = E_M + \sum_{a < b} E_{\text{rep}}^{(0)}(ab) + \sum_{a < b < c} \Delta E(abc). \quad (8)$$

As in the Born-Mayer model, polarization effects are

not considered, neither for stability nor for the evaluation of elastic constants. To establish the connection between the perturbation treatment and the Born-Mayer model, the total (first- and second-order) pair energy $E^{(0)}$ for each triplet (abc) of ions is written as

$$E^{(0)} = E_{\text{rep}}^{(0)} + E_{\text{attr}}^{(0)},$$

where $E_{\text{attr}}^{(0)} = E_{\text{attr}}^{(0)}(ab) + E_{\text{attr}}^{(0)}(ac) + E_{\text{attr}}^{(0)}(bc)$ is the van der Waals nonexchange attraction for the triplet and $E_{\text{rep}}^{(0)} = E_{\text{rep}}^{(0)}(ab) + E_{\text{rep}}^{(0)}(ac) + E_{\text{rep}}^{(0)}(bc)$ is the remainder of the pair energy. From the approximate equality (7) we obtain, for each triplet,

$$\begin{aligned} \Delta E &= \frac{\Delta E_1}{E_1^{(0)}} (E_{\text{rep}}^{(0)} + E_{\text{attr}}^{(0)}) \\ &= \frac{\Delta E_1}{E_1^{(0)}} E_{\text{rep}}^{(0)} \left(1 + \frac{E_{\text{attr}}^{(0)}}{E_{\text{rep}}^{(0)}} \right). \quad (9) \end{aligned}$$

The expression for the static lattice energy reads, from (8) and (9),

$$\begin{aligned} E_{\text{st}} &= E_M + \sum_{a < b} E_{\text{rep}}^{(0)}(ab) \\ &+ \sum_{a < b < c} \left[\frac{\Delta E_1}{E_1^{(0)}} E_{\text{rep}}^{(0)} \left(1 + \frac{E_{\text{attr}}^{(0)}}{E_{\text{rep}}^{(0)}} \right) \right] (abc), \quad (10) \end{aligned}$$

where the *relative* first-order three-ion interaction $\Delta E_1/E_1^{(0)}$ is evaluated for each triplet in the effective-electron Gaussian model. Clearly, the *absolute* quantities $E_{\text{rep}}^{(0)}(ab)$ and $E_{\text{attr}}^{(0)}(ab)$ cannot be obtained on the basis of this model. Instead, we adopt the following approximation: For each pair (ab), $E_{\text{rep}}^{(0)}(ab)$ is assumed to be proportional, by a scaling factor α , to the first-order Gaussian pair energy $E_1^{(0)}(ab)$, i.e., $E_{\text{rep}}^{(0)}(ab) = \alpha E_1^{(0)}(ab)$, where α is at most a slowly varying function of βR and γ for the values of interest for these variables. The static lattice energy, as a function of α , is then

$$\begin{aligned} E_{\text{st}} &= E_M + \alpha \left\{ \sum_{a < b} E_1^{(0)}(ab) \right. \\ &\left. + \sum_{a < b < c} \left[\Delta E_1 \left(1 + \frac{E_{\text{attr}}^{(0)}}{E_{\text{rep}}^{(0)}} \right) \right] (abc) \right\}. \quad (11) \end{aligned}$$

Equation (11) contains the unknown quantities α and, for each triplet, the ratio $E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ between the attractive and repulsive pair interactions. If the values of the ratio $E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for each triplet can be determined, then the parameter α is calculated by using the equilibrium condition $(\partial E_{\text{st}}/\partial R)_{R=R_0}=0$, where R_0 is the observed nearest-neighbor distance for the crystal in its stable structure.

No *a priori* calculation exist for the ratio $E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for any given triplet of ions, an empirical procedure must be adopted. In view of the short-range character of the pair interactions at the separations

considered and of the fact that practically all isosceles triangles in the structures considered have an opening $\theta > 60^\circ$ at the reference ion, a value for $E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ can be assigned to a shell of ions around a reference ion instead of separately to each triplet with two ions of that shell. Consequently, the value of $1 + E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ is positive if an ion of the shell considered and the reference ion repel each other and negative if this interaction is attractive. The transition from positive to negative values of $1 + E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ must be consistent in that it is the same function of the interionic separation for ions of the same kind in different salts, e.g., for chlorine ions in all of the chlorides, etc.

It is possible to select a set of values for $1 + E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ satisfying consistently the above conditions and yielding good agreement with experimental values for both transition pressures and the deviations from the Cauchy relation $c_{13} = c_{44}$. Detailed examples will be given in Sec. 4.

Having determined α from the equilibrium condition applied to the stable structure,²³ this value is then used to calculate E_{st} for the alternative structures and the pressure of transition to a structure with higher coordination number. Neglecting thermal free energy, the transition pressure is determined from the equality²⁴

$$P_I V^I + E_{\text{st}}^I = P_{II} V^{II} + E_{\text{st}}^{II}, \quad (12)$$

where I and II denote the two crystal structures; the (small) change in nearest-neighbor distance at transition is not considered.

To establish the formalism for the calculation of elastic constants, consider any two lattice points a and b . Their Cartesian coordinates in the initial, unstrained state are a_i, b_i , with $i = 1, 2, 3$. The distance R_{ab} between these lattice points in the strained crystal can be expressed in terms of the differences $b_i - a_i$ and of the six Lagrangian components e_k ($k = 1, 2, \dots, 6$) of the strain tensor. Limiting ourselves to terms linear in e_k , this relation is

$$R_{ab}^2 = (b_1 - a_1)^2(1 + 2e_1) + (b_2 - a_2)^2(1 + 2e_2) + (b_3 - a_3)^2(1 + 2e_3) + 2(b_2 - a_2)(b_3 - a_3)e_4 + 2(b_1 - a_1)(b_3 - a_3)e_5 + 2(b_1 - a_1)(b_2 - a_2)e_6. \quad (13)$$

The general expression for the elastic constants (adiabatic stiffness constants), neglecting zero-point vibrations and thermal energy, is given by

$$C_{ij} = \frac{1}{V} \frac{\partial^2}{\partial e_i \partial e_j} E_{\text{st}}, \quad i, j = 1, 6 \quad (14)$$

where V is the molar volume of the crystal and where the derivatives are understood to apply for the initial stress-free state.

²³ The derivatives of α and of $E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ with respect to R are taken to be small relative to those of $E_1^{(0)}(ab)$ and $\Delta E_1(abc)$.

²⁴ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Chap. III.

For crystals of hexagonal symmetry there are only five independent elastic constants, namely, $c_{11}, c_{12}, c_{13}, c_{33}$, and c_{44} ; the corresponding Cauchy relations are $c_{11} = 3c_{12}$ and $c_{13} = c_{44}$. In case of cubic symmetry, the independent elastic constants are c_{11}, c_{13} , and c_{44} ; there is then only one Cauchy relation, namely, $c_{13} = c_{44}$.

For the special case in which E_{st} contains pair interactions only, the validity of the Cauchy relations is immediately verified by making use of (13) in carrying out the derivations. [Note added in proof. In the structures B3 and B4 to be considered later we will neglect the contribution to the deviation from the Cauchy relations arising from internal strain due to lack of inversion symmetry. In other words, we neglect in these two structures under strain the relative displacement of the two interpenetrating sublattices.] The equalities also hold, in view of the condition of no initial stress,^{9,25} if (13) is complemented by terms quadratic in the strain components e_k . To calculate the deviations from the Cauchy relations in the case of infinitesimal strains, we are then left to consider only the three-ion component ΔE_{st} of the static lattice energy; the corresponding equations are

$$c_{13} - c_{44} = \frac{1}{V} \left(\frac{\partial^2}{\partial e_1 \partial e_3} - \frac{\partial^2}{\partial e_4^2} \right) \Delta E_{\text{st}}, \quad (15)$$

$$c_{11} - 3c_{12} = \frac{1}{V} \left(\frac{\partial^2}{\partial e_1^2} - 3 \frac{\partial^2}{\partial e_1 \partial e_2} \right) \Delta E_{\text{st}}. \quad (16)$$

It is important to remark that in the case of finite strain and in the presence of many-ion interactions the contribution of the pair potential to $c_{13} - c_{44}$ and to $c_{11} - 3c_{12}$ is not identically zero, as the crystal is not in equilibrium under pair interactions alone. We have verified that this contribution is negligibly small (always smaller than 1%) with respect to that of the three-ion component.

4. NUMERICAL RESULTS AND DISCUSSION

The expressions (11) for E_{st} and (15) for $c_{13} - c_{44}$ are the basic equations for the evaluation of the static lattice energy and the deviations from the Cauchy relation for alkali halide crystals. For each alkali halide, the expression (11) was evaluated, for the structures B1, B2, B3, and B4, using the value of the scaling factor α determined from the equilibrium condition applied to the stable structure. The structures B3 and B4 have coordination number four; in B3 (sphalerite) the sublattices are fcc, whereas, in B4 (wurtzite) they are hexagonal close packed. Although B3 and B4 are not observed for alkali halides, we have included them in the stability analysis to assess B1, B2 stability with respect to B3 and B4. The calculated deviations from the Cauchy relation always refer to the stable structure.

²⁵ C. Zener, Phys. Rev. 71, 323 (1947).

TABLE I. Comparison between theoretical and experimental results. The columns list, successively, for each salt, the dimensionless parameters βR_0 and γ , the experimental value U_{expt} of the static lattice energy together with the theoretical values U_{BM} of the Born-Mayer model and E_{st} calculated, for the stable structure, from Eq. (11) of the present work, the observed pressure of transition P_t from B_1 to B_2 , as well as the theoretical values obtained by the Born-Mayer and the present model, and, finally, the experimental (low-temperature) deviations $c_{13}-c_{44}$ from the Cauchy relation between elastic constants and the calculated value for the stable structure.

	βR_0	γ	U_{expt} Ref. a	U_{BM} Ref. b	U_{st}	$\delta(B_2-B_1)$ kcal/mole	$\delta(B_4-B_1)$ kcal/mole	$P_t(\text{expt})$	$P_t(B-M)$ Ref. c	$P_t(\text{calc})$	$(c_{13}-c_{44})_{\text{expt}}$ 10 ¹¹ dyn cm ⁻²	$(c_{13}-c_{44})_{\text{calc}}$
LiF	1.88	7.72	-242.3	-254	-258	27.8	1.1	...	300	517	-2.25 ± 0.33 ^d	-2.316
LiCl	1.44	22.00	-198.9	-196	-191	26.0	1.1	...	140	231	{ -0.422 ± 0.114 ^e -0.585 ± 0.066 ^f }	-0.262
LiBr	1.32	29.00	-189.8	-184	-175	23.9	0.9	...	105	189	{ (-0.03) ^{g,h} (+0.05) ^{g,h} }	-0.011
LiI	1.26	38.00	-177.7	-169	-158	22.6	-2.0	...	68	127	{ -0.609 ± 0.115 ^e -0.705 ± 0.046 ⁱ }	+0.057
NaF	2.16	1.54	-214.4	-219	-222	8.9	6.7	...	200	109	{ -0.208 ± 0.057 ^e -0.145 ± 0.048 ^j }	-0.647
NaCl	1.57	4.34	-182.6	-182	-178	10.0	5.9	...	74	68	{ -0.084 ± 0.050 ^e +0.017 ± 0.057 ^k }	-0.100
NaBr	1.43	5.88	-173.6	-173	-166	15.2	6.2	...	53	86	{ +0.014 ± 0.068 ^e +0.180 ± 0.045 ^m }	-0.059
NaI	1.35	7.69	-163.2	-159	-151	17.4	5.9	...	44	78	{ -0.123 ± 0.189 ^e -0.148 ± 0.006 ^{n,o} }	+0.010
KF	1.91	1.70	-189.8	-193	-189	1.8	3.0	14.6 ^l	88	14.1	{ +0.014 ± 0.068 ^e +0.180 ± 0.045 ^m }	+0.203
KCl	1.75	1.66	-165.8	-166	-157	3.5	4.3	{ 19.68 ⁿ 19.22 ^p }	74	16.9	{ +0.156 ± 0.032 ^e +0.179 ± 0.021 ^f }	-0.151
KBr	1.58	2.25	-158.5	-158	-148	4.4	3.8	{ 18.05 ⁿ 17.43 ^q }	59	18.6	{ +0.0655 ± 0.024 ^e +0.076 ± 0.023 ^u }	-0.049
KI	1.48	2.94	-149.9	-148	-138	4.8	4.9	{ 17.85 ⁿ 17.34 ^q }	49	16.6	{ +0.068 ^{r,s} +0.076 ± 0.023 ^u }	-0.019
RbF	1.69	2.43	-181.4	-183	-178	1.5	4.7	6.2 ^l	68	10.3	{ +0.068 ^{r,s} +0.076 ± 0.023 ^u }	-0.031
RbCl	1.83	1.16	-159.3	-159	-150	1.0	2.3	{ 4.90 ⁿ 5.21 ^p }	39	4.3	{ +0.0655 ± 0.024 ^e +0.076 ± 0.023 ^u }	+0.156
RbBr	1.64	1.57	-152.6	-152	-142	1.4	2.3	{ 4.51 ⁿ 4.18 ^q }	30	5.4	{ +0.0655 ± 0.024 ^e +0.076 ± 0.023 ^u }	+0.100
RbI	1.54	2.05	-144.9	-143	-132	1.6	1.8	{ 3.97 ⁿ 3.59 ^q }	22	4.8	{ +0.068 ^{r,s} +0.076 ± 0.023 ^u }	+0.114
CsF	1.51	3.46	-172.5	-175	-164	3.6	2.4	19.7 ^l	35	20.0	{ +0.023 ± 0.125 ^t +0.036 ± 0.023 ^u }	+0.083
CsCl	1.79	1.23	-155.4	-150	-140	-1.7	4.8				{ +0.023 ± 0.125 ^t +0.036 ± 0.023 ^u }	+0.021
CsBr	1.78	1.10	-149.4	-143	-133	-1.8	4.2				{ +0.023 ± 0.125 ^t +0.036 ± 0.023 ^u }	+0.034
CsI	1.66	1.44	-142.4	-135	-125	-1.6	4.2				{ +0.023 ± 0.125 ^t +0.036 ± 0.023 ^u }	-0.033

^a See Ref. 2.

^b See Ref. 22.

^c R. B. Jacobs, Phys. Rev. **54**, 468 (1938).

^d C. V. Briscoe and C. F. Squire, Phys. Rev. **106**, 1175 (1957).

^e See Ref. 4.

^f B. J. Marshall, D. O. Pederson, and G. G. Dorris, J. Phys. Chem. Solids, **28**, 1061 (1967).

^g Room-temperature value.

^h K. Spangenberg and S. Haussühl, Z. Krist. **109**, 4 (1957).

ⁱ See Ref. 12.

^j R. O. Fugate and D. E. Schuele, J. Phys. Chem. Solids **27**, 493 (1966).

^k R. N. Clayton and B. Marshall, Phys. Rev. **120**, 332 (1960).

^l C. Pistorius and H. Snyman, Z. Physik. Chemie (Frankfurt) **43**, 1 (1964).

^m B. J. Marshall and R. E. Miller, J. Appl. Phys. **38**, 4749 (1967).

ⁿ C. E. Weir and G. J. Piermarini, Ref. 1.

^o M. H. Norwood and C. V. Briscoe, Phys. Rev. **112**, 45 (1958).

^p C. W. Pistorius, J. Phys. Chem. Solids **25**, 1477 (1964).

^q C. W. Pistorius, J. Phys. Chem. Solids **26**, 1003 (1965).

^r Extrapolated.

^s Z. P. Chang, G. R. Barsch, and D. L. Miller, Phys. Status Solidi, **23**, 577 (1967).

^t B. J. Marshall, Phys. Rev. **121**, 72 (1961).

^u J. Vallin, O. Beckman, and K. Salama, J. Appl. Phys. **35**, 1222 (1964).

To perform the three-ion lattice sums occurring in (11) and (15), it is convenient to denote a central anion by A_0 , a central cation by C_0 . Anions in the i th anion shell around a central ion are denoted by A_i , the corresponding cations, by C_i . The triplets of smallest dimension in the four structures are then of the type $A_0C_1C_1$ or $C_0A_1A_1$, followed by $A_0A_1A_1$ and $C_0C_1C_1$, respectively, etc. Triplet configurations for the four structures considered have been listed previously.^{15,16}

The results for crystal stability and the deviations from the Cauchy relation $c_{13}=c_{44}$ can be understood on the basis of a few qualitative criteria. We recall that the sign of the quantity $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for each shell of ions depends on whether an ion from that shell and the central ion attract or repel each other. In the simplest crystal stability problem, that of the rare-gas solids, only the first shell of atoms must be considered for evaluating the three-atom energy. The value of

$1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for that shell is clearly negative and it was shown^{26,27} that this fact alone decides the relative stability for heavy rare-gas solids in favor of a fcc configuration. Estimating a value of -1 for the above quantity on the basis of a Lennard-Jones (6,12)-pair potential resulted, in addition to the correct stable structure, in good quantitative agreement with the measured stacking-fault energy.²⁷

For alkali halide solids, the situation is similar. Because of electrostatic compression, however, the first few shells of ions and a central ion repel each other, so that we must start with positive values for the quantity $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ in considering consecutive shells around a central ion.

Stability criteria for the different structures can be given by considering the net effect of the contributions

²⁶ L. Jansen, Phys. Rev. **135**, A1292 (1964).

²⁷ E. Lombardi and L. Jansen, Phys. Rev. **167**, 822 (1968).

TABLE II. Relations between the values of the shell quantity $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for different shells of ions in alkali halide solids and the dimensionless distance βR to the central ion, for anion-anion^a and cation-cation interactions. For each value of $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$, lower and upper limits of βR , for which this value applies, are given.

Ions \ $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$	0.5	0.25	-0.25	-0.5	-1	-1.5	-2
Fl	2.17-2.49	2.65-3.07	3.24 and 3.26		3.44-3.52		>3.72
Cl		1.50-2.03	2.11-2.29	2.35-2.47		2.52-2.58	>2.61
Br		1.36-2.05		2.16-2.25	2.32-2.36		>2.52
I		1.27-1.92		2.05-2.09	2.17-2.21	2.34	>2.41
K ^b	2.20				2.64-3.11		>3.82
Rb	1.95		2.27-2.39	2.54		2.76-2.90	>3.12
Ce		1.74-2.07	2.13 and 2.15	2.30	2.46		>2.53

^a In the case of anion-anion interactions also the distances βR arising in the silver and copper halides are already taken into account.

^b Potassium-potassium interactions are of importance only for the fluoride.

from different shells as a function of the parameters γ and βR and of the different triplet configurations. For example, the condition for stability of the $B2$ structure¹⁵ is that γ must be close to 1 and $\beta R > 1.6$.

Similar criteria determine the sign of the difference $c_{13}-c_{44}$ between elastic constants in cubic structures. If γ is close to 1 (ions of similar size), then we find that the contribution to $c_{13}-c_{44}$ from a given shell is *negative* if an ion of that shell and the central ion *repel* each other; it is *positive* if this pair interaction is *attractive*. For large values of γ (the cation much smaller than the anion) the same rules apply with regard to the anion shells around a central anion.

As an example, we consider $c_{13}-c_{44}$ for lithium fluoride ($\beta R_0 = 1.88$, $\gamma = 7.7$) and lithium iodide ($\beta R_0 = 1.26$, $\gamma = 38$). In LiF, the principal contributions arise from triplets of the types $C_0A_1A_1$ and $A_0A_1A_1$ at $\beta R = 1.88$ and 2.66, respectively. Both shells are in the repulsive field of the central ion (the fluorine ion is isoelectronic with neon; for neon the pair potential changes sign at $\beta R \approx 3$), consequently, $c_{13}-c_{44}$ is negative. In LiI, on the other hand, the sign of $c_{13}-c_{44}$ is determined by contributions from triplets of the types $A_0A_1A_1$ at $\beta R = 1.78$ and $A_0A_2A_2$ at $\beta R = 2.52$. The second anion shell is certainly in the attractive field of the central anion (the iodine ion is isoelectronic with xenon, for which the pair potential changes sign at $\beta R \approx 1.9$), consequently, the contribution from this shell to $c_{13}-c_{44}$ is positive. It is thus to be expected that $c_{13}-c_{44}$ will be less negative for LiI than for LiF, in agreement with experiment. For ions of similar size (γ small) several shells will contribute to this difference, some with positive and some with negative sign. This will lead to small values of $c_{13}-c_{44}$ of either sign, which is borne out by the experimental results.

For the numerical analysis, several possible sets of values for the quantities $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for different shells and different ions were selected, applying the above criteria. The results which are in best agreement with experiments *both* for polymorphism and for the differences $c_{13}-c_{44}$ are given in Table I. This Table contains, for each salt, the values of βR_0 and γ , the

experimental values and those calculated on the basis of the Born-Mayer and the present model of the static lattice energy, the pressure of transition from $B1$ to $B2$ and the deviation $c_{13}-c_{44}$ from the Cauchy relation. The calculated energy differences $\delta(B2-B1)$ and $\delta(B4-B1)$ are also given.

The results are seen to be in good general agreement with experiment, both for polymorphism and $c_{13}-c_{44}$. It is to be noted that the calculated values of the static lattice energy are generally in less than good agreement with experimental values than those obtained with the Born-Mayer model. This may be caused by the fact that the effective potential in the Born-Mayer treatment is determined empirically from the known equilibrium distance and the compressibility. In view of the occurrence of three-ion interactions in the present model, the expression connecting the compressibility and the potential is too complicated to be of use. The present analysis has been undertaken primarily to account for observed polymorphism and deviations from the Cauchy relation, for which an effective potential model fails.

Regarding stability, the only exception is LiI, which is predicted to be more stable in the $B4$ configuration, whereas, the experimental stable structure is $B1$. The discrepancy can be removed by assuming that at the small βR values involved ($\beta R_0 = 1.26$), short-range attractive (second-order) pair interactions between the nearest iodine ions invalidate the assumption $E_{\text{rep}}^{(0)}(ab) = \alpha E_1^{(0)}(ab)$ for constant α . If such is the case, then the pair repulsion is less than the calculated value. It is found that a reduction of the iodine-iodine first-order Gaussian repulsion by 10% restores the stability of the $B1$ configuration by 2 kcal/mole. As will be shown in the following paper, this reduction of the pair repulsions plays a dominant role for stability of ionic solids where the cation has a complete d shell of electrons.

The values of $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for the different shells of ions in the different alkali halides are given in Table II, as a function of the βR values which occur for the alkali halides in the structures $B1$, $B2$, $B3$, and $B4$. To simplify the table we list, for each value of

$1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$, the lower and upper limits of βR for which this value applies. The values pertaining to anion-anion pair interactions are given for all halides (including the silver and copper halides to be discussed in the following paper), those for cation-cation interactions pertain to potassium,²⁸ rubidium, and cesium only. The corresponding values for lithium and sodium are of little importance in view of the relative smallness of these cations.

The values listed in Table II can in part be derived from the known pair potentials between the isoelectronic rare-gas atoms.

For mixed triplets of the types $A_0C_iC_i$ and $C_0A_iA_i$, the following procedure was adopted. If $\gamma \approx 1$, then the same value of $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ can be assigned to both these types of triplet for a fixed value of i . On the other hand, if $\gamma \gg 1$ (lithium salts), then we must consider only triplets of the type $C_0A_iA_i$, the contributions from triplets $A_0C_iC_i$ being negligibly small. The most important contributions result in all cases from mixed triplets involving two ions of the first shell around a central ion, the value of $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for these triplets is taken as 0.5, in accordance with a previous analysis,¹⁵ except for the light fluorides (0.25 for LiF and NaF, 0.35 for KF).

To illustrate the dependence of the results for the transition pressure P_t and the difference $c_{13}-c_{44}$ on the variation of values for the quantities $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for the different shells, we give in Table III a detailed analysis for rubidium chloride. This case is of particular interest, since the energy difference between the $B1$ and $B2$ configurations is very small (less than 1% of the crystal energy); the βR and γ values are 1.83 and 1.16, respectively. In the sets of results numbered 1-3 in the Table, the quantities $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for the shells $A_0C_iC_i$ and $C_0A_iA_i$ for $i=2, 3$ up to $\beta R=4$, as well as those for $A_0A_iA_i$, $C_0C_iC_i$, for $i=4, 5$ up to $\beta R=4$ (all these shells are, of course, in the attractive field of a central ion) are $-1.0, -1.5, -2.0$, respectively. In the sets numbered 4-6, the same variations are applied, with the shell value for $C_0C_1C_1$ in $B1$ taken -2.0 instead of -1.5 (as from Table II). All other values are the same as in Table II. The results show that RbCl is definitely stable in $B1$ and that $c_{13}-c_{44}$ is positive. Moreover, P_t and $c_{13}-c_{44}$ change in the same manner under these variations. The experimental values for P_t and $c_{13}-c_{44}$ are 4.9 kbar and 0.16 ± 0.03 (or 0.18 ± 0.02) 10^{11} dyn/cm².

5. CONCLUDING REMARKS

In the present analysis, we have shown that the relative stability of alkali halide crystals and the observed low-temperature deviations from the Cauchy relation $c_{13}=c_{44}$ for cubic structures can be interpreted on the basis of a Born-Mayer model supplemented by

TABLE III. Calculated values, for rubidium chloride, of the static lattice energy E_{st} , the differences in energy $\delta(B2-B1)$ and $\delta(B4-B1)$, the pressure of transition P_t , and the difference ($c_{13}-c_{44}$) as a function of different sets of values for the quantities $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ as given in the text.

Set	E_{st} eV	$\delta(B2-B1)$ kcal/mole	$\delta(B4-B1)$ kcal/mole	P_t eV	$(c_{13}-c_{44})$ eV
1	-149.9	0.51	2.23	2.20	0.142
2	-150.0	0.99	2.29	4.28	0.156
3	-150.1	1.49	2.34	6.44	0.166
4	-150.2	-0.02	2.00	...	0.189
5	-150.3	0.45	2.05	1.93	0.203
6	-150.4	0.94	2.11	4.04	0.211

non-Coulombic three-ion exchange interactions. The latter were evaluated, in first and second orders of perturbation theory, on the basis of a Gaussian effective-electron model. In the three-ion component of the crystal energy, each shell of ions around a central ion in the four structures $B1, B2, B3$, and $B4$ is weighted by a quantity $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$, containing only pair interactions between the ions.

Regarding crystal stability the results are largely the same as those given in a previous analysis,¹⁵ where we compare only the $B1$ and $B2$ structures and where the scaling parameter α of the pair repulsion was determined in a different manner, using the experimental values of the crystal energy (the agreement for the pressure of transition P_t from $B1$ to $B2$ is now considerably better for some salts, as a result of the present more detailed analysis). Including the $B3, B4$ structures, the stability sequence for the light alkali halides is $B1 > B3, B4 > B2$, whereas, for the rubidium and cesium salts the order is $B1 > B2 > B3, B4$ or $B2 > B1 > B3, B4$. We recall that the original Born-Mayer model gives, for all halides, the sequence $B1 > B2 > B3, B4$ in the range of values for the exponent p in the pair repulsion R^{-p} as obtained from compressibility data. With respect to the Born-Mayer treatment, the present model introduces two additional elements, namely, the different size of the ions (represented by the Gaussian ratio γ between the β parameters of cation and anion) and the three-ion interactions. The three-ion component amounts to a few percent of the static lattice energy, it is always attractive in the stable structure. For the cesium halides stable in $B2$ the three-ion energy is practically zero in a $B1$ configuration and repulsive in $B3$ and $B4$. A more complete discussion of relative stability for these four structures has been given previously.²²

Regarding the deviations from the Cauchy relation $c_{13}=c_{44}$, the good agreement between theoretical and experimental values suggests that the polarization effect considered by Herpin⁷ and Löwdin's exchange charge-Coulomb field interactions⁹ have little influence on the values of $c_{13}-c_{44}$. As was mentioned already in the Introduction, Herpin's calculation cannot be carried to near neighbors of a central ion since then exchange effects must play a role. Also, Löwdin's calculation should be extended to second order of perturbation

²⁸ Potassium-potassium interactions are of importance only for the fluoride.

theory before conclusions may be drawn. We are at present performing such an analysis on a model basis.

The necessity of empirically assigning values for the shell quantities $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ in the evaluation of the three-ion energy derives merely from the fact that

no *a priori* calculations exist for the *pair potentials* between two ions. In the present calculation, the three-ion interactions are determined relative to the pair forces; to arrive at absolute results the pair interactions must, therefore, be estimated.

Influence of Short-Range Three-Ion Interactions on Polymorphism and Elastic Constants of Simple Solids. II. Compounds with Closed d -Shell Cations

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The analysis given in the previous paper of polymorphism and low-temperature deviations from the Cauchy relation $c_{13}=c_{44}$ between the elastic constants of alkali halide solids is extended to ionic crystals of composition AX whose cations possess closed outer d shells of electrons, i.e., monovalent copper and silver, and divalent zinc and cadmium. The Born-Mayer model is again taken as a basis, supplemented by three-ion, exchange, non-Coulombic interactions in first and second orders of perturbation theory. It is found that attractive, exchange, cation-cation, and cation-anion pair interactions together with the three-ion forces explain polymorphism and the deviations from the Cauchy relations in cubic and hexagonal structures.

1. INTRODUCTION

IN the previous paper¹ (hereafter referred to as I), we analyzed polymorphism and the low-temperature deviations from the Cauchy relation $c_{13}=c_{44}$ between elastic constants of cubic crystals for solids of the alkali halides. In the present analysis, we will apply a similar method to solids of composition AX whose cations have closed shells of outer d electrons, i.e., to cations of copper and silver, zinc and cadmium. The analysis given in I was based on a Born-Mayer type of model supplemented by three-ion, exchange, non-Coulombic interactions. The three-ion interactions were evaluated in first and second orders of perturbation theory on the basis of an effective-electron approximation, replacing the electron distribution of each (closed-shell) ion by one effective electron. The charge distribution of this electron was chosen to be of Gaussian form; electron spins on different ions are parallel to avoid valence binding. The three-ion forces were evaluated relative to the pair interactions; these relative quantities follow simple laws with respect to the geometry of the triangles formed by triplets of ions. Only triplets of ions forming isosceles triangles with a reference ion must be considered, so that the total three-ion energy can be evaluated by summing over the different *shells* of ions around the reference ion. The results of the analysis were found to be in good agreement with experimental data for both relative stability of the four structures $B1(\text{NaCl})$, $B2(\text{CsCl})$, $B3(\text{sphalerite})$, and $B4(\text{wurtzite})$ considered

and for the low-temperature deviations from the Cauchy relation $c_{13}=c_{44}$ between the elastic constants of cubic structures (for alkali halide crystals, only the cubic structures $B1$ and $B2$ are observed).

The main reason for treating solids with closed d -shell cations separately from the alkali halides and from the II-VI and III-V compounds, whose ions are isoelectronic with rare-gas atoms, lies in the fact that from all the previous work existing in the literature^{2,3} (for an extensive review of the subject see Tosi⁴) it has been concluded that these salts are much less ionic than those of the alkali halides. The motivation of this conclusion is that the experimental lattice energies for the copper and silver halides are as large as, or even larger than, the Madelung energy. In addition, the crystal structures found for these compounds are $B1$, $B3$, and $B4$ and not $B1$, $B2$ as for the alkali halides; this indicates that the interactions between the ions might be different. The available calculations of the static lattice energy for these salts have all been based on the Born-Mayer model, where the static lattice energy is written as a sum of three components, namely, the Madelung energy E_M , the repulsive (overlap) energy (which, in its simplest form, is given by $E_{\text{rep}} = Be^{-R/\rho}$, where B and ρ are the repulsive parameters and R is the nearest-neighbor distance), and, finally, the van der Waals energy $E_{\text{vdW}} = -C/R^6 - D/R^8$, where C and D are linear combinations of the van der Waals coefficients for interactions of the various ion pairs, weighted by appropriate lattice sums.⁴ More refined expressions

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¹ E. Lombardi, L. Jansen, and R. Ritter, Phys. Rev. preceding paper, 185, 1151 (1969).

² J. E. Mayer, J. Chem. Phys. 1, 327 (1933).

³ J. E. Mayer and R. B. Levy, J. Chem. Phys. 1, 647 (1933).

⁴ M. P. Tosi, Solid State Phys. 16, 1 (1964).

exist for the repulsive part of the Born-Mayer potential (for a detailed analysis we again refer to Tosi⁴) in which anion-anion and cation-cation interactions are explicitly taken into account. Because of the lack of necessary experimental data, there remain many uncertainties in such a procedure. Alternatively, the values of ρ determined for alkali halides have been simply transferred to copper and silver halides; for the reliability of this procedure, see Ref. 4. In addition, Lynch⁵ has concluded from a careful analysis that the value of the van der Waals dipole-dipole coefficient C as calculated from optical data is without meaning. On this basis, it appears difficult to assess the validity of the Born-Mayer model as applied to solids whose cations have a complete outer shell of d electrons.

The cohesive energies calculated on the basis of the Born-Mayer model are systematically less negative than the experimental values, with relatively large discrepancies for the salts crystallizing in the B3 or B4 structure. Mayer² suggested that these discrepancies are due to homopolar (covalent) bonding between the ions. A quantitative verification of this suggestion necessitates an *a priori* calculation which is at present too complex a problem to be carried through.

In the present analysis, we will adopt an approach which does not involve homopolar bonding between the ions. As a basis we assume again the validity of the Born-Mayer model, supplemented, as in I, by non-Coulombic three-ion exchange forces. In addition, we must introduce short-range (second-order) attractive cation-cation and cation-anion interactions arising because of the presence of a complete outer shell of d electrons whose excited states lie considerably lower than the excited states of an ion with rare-gas configuration. The expression for the static lattice energy will then contain the Madelung energy, the pair repulsion due to anion-anion interactions, as in the case of the alkali halides and of the II-VI and III-V compounds (the anions considered are isoelectronic with rare-gas atoms), the pair repulsion, the short-range second-order attraction for cation-cation and cation-anion interactions, and, finally, the three-ion non-Coulombic exchange forces.

Before proceeding to the explicit formalism we remark that qualitative support for the above assumptions can be obtained on the basis of the general results for the elastic constants of the alkali halide crystals. It was found in I that the deviation from the Cauchy relation $c_{13}-c_{44}$ for cubic crystals can be calculated by summing over three-ion contributions arising from consecutive shells around a central ion. The contribution to $c_{13}-c_{44}$ is of negative sign if an ion of the shell considered and the central ion repel each other; it is positive when this pair interaction is attractive. The introduction in the above model of short-range attractive forces for cation-cation and cation-anion pairs will favor the occurrence

TABLE I. Gaussian parameters and stable structures of all the salts considered.

Salt	βR_0	γ	Stable structure ^a	Salt	βR_0	γ	Stable structure ^a
CuF	1.47	1.37	B3	AgF	1.48	2.44	B1
CuCl	1.31	2.06	B3, B4	AgCl	1.54	1.16	B1
CuBr	1.18	2.79	B3, B4	AgBr	1.38	1.57	B1
CuI	1.10	3.65	B3, B4	AgI	1.17	2.05	B3, B4
ZnO	1.19	1.78	B4	CdO	1.41	1.00	B1
ZnS	1.04	3.23	B3, B4	CdS	1.13	1.82	B3, B4
ZnSe	0.99	3.88	B3, B4	CdSe	1.07	2.18	B4
ZnTe	0.93	5.05	B3, B4	CdTe	1.00	2.84	B3, B4

^a R. W. G. Wyckoff, *Crystal Structures* (Wiley-Interscience Publishers, Inc., New York, 1963), Chap. III.

of positive contributions to $c_{13}-c_{44}$. It is found experimentally⁶⁻⁹ that the low-temperature values of the difference $c_{13}-c_{44}$ for AgCl, ZnS, and CdS are indeed positive and large.

We will now undertake a quantitative analysis of the problem by extending the model developed in I.

2. STATIC LATTICE ENERGY

As in I, we start from the (hypothetical) free ions possessing closed shells of electrons. The interactions between the ions are calculated in first and second orders of perturbation theory, taking electron exchange into account. The static lattice energy is written as the sum of Coulombic (Madelung) and non-Coulombic components; the latter is expanded in a cluster series and terminated after three-ion contributions. The three-ion part of the interaction energy is determined for each triplet of ions in the solid, *relative* to the sum of pair interactions between the three pairs of ions forming the triplet. These relative quantities, in first and second orders of perturbation theory, are evaluated by replacing the electron distribution of each closed-shell ion of a triplet by an effective electron with a Gaussian distribution of charge.

A cation-anion pair is defined, as in I, by two Gaussian parameters, β and β' , with the convention $\beta' \geq \beta$, so that β' stands for the smaller of the two ions. The characteristic dimensionless parameters of the model are then βR_0 , where R_0 is the nearest-neighbor distance in the solid, and $\gamma = (\beta'/\beta)^2 \geq 1$. Values for β and β' can be obtained, in the case of alkali halide ions and the anions of column VI of the Periodic Table, from known diamagnetic susceptibilities χ and the β values for the corresponding isoelectronic rare-gas atoms.¹⁰ For Cu^{1+} and Ag^{1+} , the values of the Gaussian parameter were estimated by interpolation on a β - χ curve for the alkali ions; those for Zn^{2+} and Cd^{2+} were obtained

⁶ W. H. H. Shaw, J. T. Lewis, and C. V. Briscoe, *Phys. Rev.* **163**, 876 (1967).

⁷ J. Vallin, *Arkiv Fysik* **34**, 367 (1967).

⁸ A. Zarembovitch, *J. Physique* **24**, 1097 (1963).

⁹ D. Gerlich, *J. Phys. Chem. Solids* **28**, 2575 (1967).

¹⁰ E. Lombardi and L. Jansen, *Phys. Rev.* **140**, A275 (1965).

⁵ D. W. Lynch, *J. Phys. Chem. Solids* **28**, 1941 (1967).

TABLE II. Relations between the values of the shell quantity $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for different shells $A_0A_iA_i$ of divalent anions and the dimensionless distance βR to the central ion. For each value of $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$, lower and upper limits of βR , for which this value applies, are given.

Anions \ $1 + \frac{E_{\text{attr}}^{(0)}}{E_{\text{rep}}^{(0)}}$	0.5	0.25	-0.25	-0.5	-1
O	1.62-1.99	2.29-2.39	2.75-2.81	3.25	
S		1.20-2.07	2.25-2.40	...	2.60
Se		1.14-1.97	2.14-2.28	...	2.47
Te		1.07-1.86	1.99-2.14	...	2.32

by interpolating on the corresponding curve for alkali-earth ions. The interpolated β values are $0.8 \text{ \AA}^{-1}$ for Cu^{1+} and Zn^{2+} , and $0.6 \text{ \AA}^{-1}$ for Ag^{1+} and Cd^{2+} .

The βR_0 and γ values for all the salts considered, together with their stable crystal structures, are given in Table I. The starting expression for the static lattice energy can be taken as

$$E_{\text{st}} = E_M + \sum_{a < b} \mathcal{E}^{(0)}(ab) + \sum_{a < b < c} \Delta E(abc), \quad (1)$$

where, as in I, E_M is the Madelung energy and $\Delta E(abc)$ is the three-ion contribution of the triplet (abc) to the lattice energy. The pair energy $\mathcal{E}^{(0)}(ab)$ is defined as the total (first- plus second-order) interaction energy for the pair (ab) minus the nonexchange van der Waals attraction. This quantity was denoted in I by $E_{\text{rep}}^{(0)}(ab)$; the new symbol is necessary for salts with closed d -shell cations since $\mathcal{E}^{(0)}(ab)$ is not always a repulsive energy in view of the occurrence of short-range attractive cation-cation and cation-anion forces. Again, as in I, we do not take account of pair van der Waals attractions in the static lattice energy. For anion-anion pairs, $\mathcal{E}^{(0)}(ab) = E_{\text{rep}}^{(0)}(ab)$. From the approximate equality

$$\frac{\Delta E_1}{E_1^{(0)}} = \frac{\Delta E_2}{E_2^{(0)}} = \frac{\Delta E}{E^{(0)}},$$

we can express the three-ion contribution of each triplet (abc) as

$$\Delta E = \frac{\Delta E_1}{E_1^{(0)}} \mathcal{E}^{(0)} \left(1 + \frac{E_{\text{attr}}^{(0)}}{\mathcal{E}^{(0)}} \right).$$

As in I, the relative first-order three-ion energy $\Delta E_1/E_1^{(0)}$ is evaluated for each triplet in the effective-electron Gaussian model and the absolute quantities $\mathcal{E}^{(0)}$ and $E_{\text{attr}}^{(0)}$ will be determined in a semiempirical way.

For alkali halide crystals we proceeded in I by assuming that $E_{\text{rep}}^{(0)}(ab) = \alpha E_1^{(0)}(ab)$, with α a scaling parameter connecting the true pair repulsion and the first-order energy, $E_1^{(0)}(ab)$, the latter quantity evaluated on the basis of the Gaussian model. The parameter α was taken the same for all pairs of ions. The basic difference between the present analysis and

that given in I lies in the assumption, consistent in the framework of the model, that this scaling procedure is not valid for the Cu, Ag, Zn, and Cd salts in view of the occurrence of important short-range attractions for cation-cation and cation-anion pairs. This "reduction of the pair repulsion" can formally be written as

$$\mathcal{E}^{(0)}(ab) = \omega \alpha E_1^{(0)}(ab), \quad (2)$$

with $\omega = 1$ for anion-anion, $\omega < 1$ for cation-cation and cation-anion pairs. In this way, the present analysis is very similar to that given in I; the only difference being the occurrence of the parameter ω .

In principle, ω is a different quantity for each cation-cation or cation-anion pair in the pair-repulsion component of the static lattice energy; however, a detailed analysis taking this variation into account is too complex. Instead, we simplify the procedure by adopting a same average value ω for cation-cation and cation-anion pairs.

The expression for the static lattice energy reads now

$$E_{\text{st}} = E_M + \sum_{a < b} \alpha \omega E_1^{(0)}(ab) + \sum_{a < b < c} \left[\frac{\Delta E_1}{E_1^{(0)}} \mathcal{E}^{(0)} \left(1 + \frac{E_{\text{attr}}^{(0)}}{\mathcal{E}^{(0)}} \right) \right] (abc). \quad (3)$$

This expression contains the two parameters α and ω , which can be determined from the equilibrium condition applied to the stable structure and from the experimental value of the compressibility of each salt considered. However, compressibility data are available only for a small number of salts, in addition, the procedure involved is inaccurate in the present case since the compressibility is inversely proportional to the second derivative of the static lattice energy. Instead, we vary ω parametrically and choose its value such that the experimental lattice energy is reproduced for each salt.

We proceed by assigning to each shell of ions a value of the quantity $(\mathcal{E}^{(0)}/\alpha E_1^{(0)})(1+E_{\text{attr}}^{(0)}/\mathcal{E}^{(0)})$; for each value of ω the parameter α is determined from the equilibrium condition applied to the stable structure. The same formalism as given in I is then used for the analysis of polymorphism and for the calculation of the deviations from the Cauchy relations. A detailed account will be given in Sec. 3.

3. NUMERICAL RESULTS AND DISCUSSION

Regarding the three-ion component of the static lattice energy, represented by the last term of Eq. (3), we note that a separate analysis must be made for the different types of triplet. For those of the type $A_0A_iA_i$ (as in I, we denote anions by A , cations by C , and index according to the numbering of shells around a central ion) the contribution is again expressed, as for alkali halides, by

$$\alpha \Delta E_1 (1 + E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)})$$

TABLE III. Comparison between theoretical and experimental results for salts stable in the $B1$ configuration.

Salt	ω	E_{at}	$\delta(B2-B1)$ kcal/mole	$\delta(B3-B1)$ kcal/mole	$\delta(B4-B1)$ kcal/mole	$P_t(\text{calc})(B1-B2)$ kbar	$(C_{12}-C_{44})_{\text{calc}}$ 10^{11} dyn cm $^{-2}$	U_{expt} kcal/mole ^a	$P_t(\text{expt})$ kbar ^b	$(C_{12}-C_{44})_{\text{expt}}$ 10^{11} dyn cm $^{-2}$
AgF	0	-209	11.4	25.2	24.3	115	2.96	-228		
AgCl	-0.3	-222	11.2	15.7	13.6	79	4.41	-215	100	{ 3.22 $\pm$ 0.03 at 4.2°K ^c 3.21 $\pm$ 0.08 at 4.2°K ^d
	-0.2	-200	13.2	8.2	6.8	93	2.78			
AgBr	-0.3	-213	8.0	14.5	12.2	50	3.85	-212	90	2.6 at 300°K ^e
	-0.2	-196	10.5	8.9	7.2	66	2.76			
CdO	-0.1	-883	56.6	8.7	2.7	660	10.97	-910		

^a Landolt-Börnstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1955), Vol. I, part 4, p. 534.

^b W. Klement and A. Jayaraman, *Progr. Solid State Chem.* 3, 289 (1967).

^c See Ref. 6.

^d See Ref. 7.

^e D. S. Tannhauser, L. J. Broner, and A. W. Lawson, *Phys. Rev.* 102, 1276 (1956).

for each triplet; the values of $1 + E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ in case of halide ions are taken directly from Table II of I. Those for the divalent anions isoelectronic with rare-gas atoms can be assigned on a similar basis; they are listed in Table II.

For all other triplets (types $A_0C_iC_i$, $C_0A_iA_i$, and $C_0C_iC_i$) we note that, if the average value of ω could be replaced by separate values $\omega(ab)$ for each ion pair, then the three-ion contribution from each such triplet would depend explicitly on the values for $\omega(ab)$. This procedure, however, is much too complicated. Instead, we vary the quantity $(\mathcal{E}^{(0)}/\alpha E_1^{(0)})(1 + E_{\text{attr}}^{(0)}/\mathcal{E}^{(0)})$ of (3) independently of ω . Physically, this procedure implies that the short-range attractive forces arising because of the closed d -shell cations are primarily effective in reducing the non-Coulombic pair energy.

It proves possible to find, for all salts, a *unique* value for each of the quantities $(\mathcal{E}^{(0)}/\alpha E_1^{(0)})(1 + E_{\text{attr}}^{(0)}/\mathcal{E}^{(0)})$ pertaining to triplets of the types $A_0C_1C_1$, $C_0A_1A_1$, and $C_0C_1C_1$, respectively, which lead to close agreement with the experimental data for both polymorphism and for the deviations from the Cauchy relations. Best agreement is obtained by assigning a value of -0.25 for triplets $A_0C_1C_1$, $+0.25$ for triplets $C_0A_1A_1$, -0.5 for $C_0C_1C_1$; these triplets give generally the most important contribution so that no further shells need be considered.

The positive value which must be chosen for triplets $C_0A_1A_1$ implies that under electrostatic compression the short-range attractive cation-anion interactions are partly counterbalanced by anion-anion repulsion. This can be seen in more detail from the explicit expression for the corresponding three-ion energy, i.e., from (2),

$$\begin{aligned} & \frac{\Delta E_1}{E_1^{(0)}} (\mathcal{E}^{(0)} + E_{\text{attr}}^{(0)}) \\ &= \alpha \Delta E_1 \left[2\omega \frac{E_1^{(0)}(C_0A_1)}{E_1^{(0)}(C_0A_1A_1)} \left(1 + \frac{E_{\text{attr}}^{(0)}(C_0A_1)}{\mathcal{E}^{(0)}(C_0A_1)} \right) \right. \\ & \quad \left. + \frac{E_1^{(0)}(A_1A_1)}{E_1^{(0)}(C_0A_1A_1)} \left(1 + \frac{E_{\text{attr}}^{(0)}(A_1A_1)}{E_{\text{rep}}^{(0)}(A_1A_1)} \right) \right], \quad (4) \end{aligned}$$

where $E_1^{(0)}(C_0A_1)$ and $E_1^{(0)}(A_1A_1)$ are the first-order perturbation energies for the cation-anion and the

anion-anion pair, respectively, and where $E_1^{(0)}(C_0A_1A_1) = 2E_1^{(0)}(C_0A_1) + E_1^{(0)}(A_1A_1)$. It follows directly that, if $E_1^{(0)}(A_1A_1)$ is not negligible with respect to $E_1^{(0)}(C_0A_1A_1)$, then this anion-anion repulsion counterbalances the short-range cation-anion attraction (for negative ω).

In Tables III-V, we list, as a function of ω , the numerical results for the crystal energy of the stable structure, its relative stability with respect to the alternative structures, the transition pressures to structures with higher coordination number than the stable one, and the deviations from the Cauchy relations, for salts which are stable, respectively, in the $B1$, $B3$, or $B4$ configuration, together with available experimental data.¹¹

The results of Tables III-V indicate that, wherever comparison with experimental data can be made, the agreement with the theoretical results is good. In particular, we note:

(1) The values of ω are found to be always negative, except in the case of AgF, CuF, ZnO, and CdO, where they are zero for the fluorides, 0.1 for ZnO and between -0.1 and zero for CdO. These small positive or slightly negative values can be attributed to the smallness of the fluorine and oxygen ions, both isoelectronic with neon. For such small anions, the cation-anion short-range attraction is relatively of less importance than in the case of the larger anions (of Cl, Br, I, S, Se, and Te).

(2) The ω values for the heavier copper salts are more negative than those for the corresponding silver salts. This is in agreement with chemical evidence according to which copper has a stronger tendency than silver to form divalent compounds.

(3) The salts stable in structures with coordination number four have practically the same energy in the two configurations $B3$ and $B4$, in accordance with experimental observations. This is a consequence of the fact that the main three-ion contributions arise from triplets $A_0C_1C_1$, $C_0A_1A_1$, and $C_0C_1C_1$, which are identical in the two structures. As the Madelung energy in the $B4$ structure is slightly larger than that of $B3$ (difference of the order of $\frac{1}{10}$ of 1%), we find a slightly higher

¹¹ In $B3$ and $B4$ we neglect possible contributions from internal strain to the elastic constants.

TABLE IV. Comparison between theoretical and experimental results for salts stable in the B3 configuration.

Salt	ω	E_{st}	$\delta(B1-B3)$	$\delta(B2-B3)$	$\delta(B4-B3)$	$P_t(B3-B1)$	$P_t(B3-B2)$	$(c_{12}-c_{44})_{calc}$	U_{expt}	$P_t(expt)$	$(c_{12}-c_{44})_{expt}$
			kcal/mole			kbar		$10^{11} \text{ dyn cm}^{-2}$	kcal/mole ^a	kbar ^b	$10^{11} \text{ dyn cm}^{-2}$
CuF	0	-255	10.7	44.1	-1.5	110	318	6.29			
CuCl	-0.2	-231	0.8	16.6	-2.0	4	58	1.80	-236	42; 55	
CuBr	-0.4	-231	14.8	25.7	-2.6	64	78	1.58	-232	47; 80	
CuI	-0.8	-226	0.8	33.8	-2.5	3	85	1.53	-231	4; 5; 30	
	-0.7	-215	3.6	36.7	-2.2	13	92	1.32			
ZnS	-0.3	-852	39.0	46.7	-1.8	199	167	2.84	-853	240	1.88 $\pm$ 0.09 ^{c,d}
	-0.2	-830	46.1	70.3	-1.7	235	251	2.52			
ZnSe	-0.6	-837	18.4	35.0	-0.9	83	110	2.12	-844	160	0.47 at 300°K
ZnTe	-0.6	-712	26.7	113.0	0.3	97	287	0.63	-808	4	0.95 at 300°K ^e
	-0.5	-702	31.5	122.0	0.2	114	309	0.59			
AgI	-0.4	-211	0.9	11.2	-3.4	2.5	23	1.76	-211	4	
	-0.3	-196	4.9	19.5	-2.7	14.4	40	1.38			
CdS	-0.1	-785	6.2	29.8	-2.6	24	83	3.59	-808	33	2.34 at 77°K ^e
	-0.4	-726	16.0	33.6	0.2	47	69	2.77			
CdTe	-0.3	-703	25.4	57.4	0.1	75	118	2.41			

^a See Ref. a Table III.
^b See Ref. b Table III.
^c See Ref. 8.
^d 0°K extrapolation.
^e D. Berlincourt, H. Jaffe, and R. L. Shiozawa, Phys. Rev. **129**, 1009 (1963).

stability of B4 at the same equilibrium nearest-neighbor distance R_0 . We note, in comparison with the B3, B4 stability problem for II-VI and III-V compounds,¹⁰ that the βR_0 values occurring for those salts are smaller and the γ values much higher than in the case of the closed d shell cations.

(4) Except for the fluorides, to be discussed below, the stability of the structure with lowest coordination number (B3 or B4) is always associated with the smallest values of βR_0 and the largest values of γ . This is due to the fact that, on one hand, the low values of βR_0 introduce more $A_0A_iA_i$ shells in the B1 structure, i.e., in the structure with higher coordination number a larger amount of three-ion repulsion is developed; on the other hand, in view of the high values of γ , the

difference in short-range attractive forces between B1 and B3, B4 is not sufficiently large to stabilize B1.

(5) Regarding the crystal stability of CuF (stable structure B3) and AgF (stable structure B1), we observe that the values of βR_0 are practically the same for the two salts. Since the copper ion is smaller than the silver ion, the cation-anion short-range attraction is less important in CuF than in AgF. On this basis, a structure with higher coordination is favored for AgF. In addition, the anion sublattice in AgF is at larger values of $\beta'R$ (β' is the Gaussian parameter for the fluorine ion) than in CuF, again favoring a crystal structure with high coordination number (higher Madelung constant).

As we have noted before, the main difference between

TABLE V. Comparison between theoretical and experimental results for salts stable in the B4 configuration.

Salt	ω	E_{st}	$\delta(B1-B4)$	$\delta(B2-B4)$	$\delta(B3-B4)$	$P_t(B4-B1)$	$P_t(B4-B2)$	$c_{12}-c_{44}$	$c_{11}-3c_{12}$	U_{expt}	$P_t(expt)$	$(c_{12}-c_{44})_{expt}$	$(c_{11}-3c_{12})_{expt}$
			kcal/mole			kbar		$10^{11} \text{ dyn cm}^{-2}$		kcal/mole ^a	kbar ^b	$10^{11} \text{ dyn cm}^{-2}$	
CuCl	-0.2	-233	3.9	20.8	2.1	20	73	1.52	-3.65	-236			
CuBr	-0.4	-235	19.1	30.9	2.7	83	93	1.35	-3.03	-232			
CuI	-0.8	-227	4.1	38.7	2.6	14	97	1.35	-2.54	-231			
	-0.7	-215	6.5	41.0	2.3	24	103	1.16	-2.17				
ZnO	0	-1007	17.2	72.2	9.4	141	414	6.03	-18.20	-965		6.26	-15.36 at 300°K ^e
	0.1	-969	34.2	109.8	7.8	280	629	4.90	-14.79				
ZnS	-0.3	-855	39.8	47.4	1.8	203	169	2.90	-6.01	-852	240	3.23	-6.77 at 300°K ^d
	-0.2	-833	47.0	70.9	1.7	239	253	2.59	-5.54				
ZnSe	-0.6	-839	17.6	33.7	0.9	79	106	2.25	-4.41	-844			
ZnTe	-0.6	-715	24.1	107.7	-0.3	87	274	0.77	-1.24	-211			
	-0.5	-705	29.1	116.8	-0.2	105	396	0.72	-1.16				
AgI	-0.4	-216	6.0	17.6	3.7	18	36	1.67	-3.79	-808	20	3.34	-7.62 at 4.2°K ^e
	-0.3	-199	9.2	25.1	2.9	27	52	1.27	-2.89				
CdS	-0.1	-788	8.8	32.4	2.6	34	90	3.82	-7.00	-800	23	2.6	-6.15 at 300°K ^f
CdSe	-0.2	-770	3.4	31.3	1.5	12	77	3.51	-5.99	-800	23	2.6	-6.15 at 300°K ^f
	-0.4	-727	14.0	30.9	-0.2	41	64	3.04	-4.65				
CdTe	-0.3	-705	23.6	49.6	0.0	69	112	2.65	-4.06				

^a See Ref. a Table III.
^b See Ref. b Table III.
^c T. B. Bateman, J. Appl. Phys. **33**, 3309 (1962).
^d J. de Klerk, J. Phys. Chem. Solids **28**, 1831 (1967).
^e See Ref. 9.
^f See Ref. c Table IV.

the present analysis for compounds with closed d -shell cations and the one presented in I for alkali halides lies in a modification of the scaling procedure $E_{\text{rep}}^{(0)}(ab) = \alpha E_1^{(0)}(ab)$ adopted in I, where $E_1^{(0)}(ab)$ is the first-order Gaussian energy and $E_{\text{rep}}^{(0)}(ab)$ is the difference between the total pair energy and the van der Waals nonexchange interaction for the pair. Instead, because of the occurrence of short-range attractive pair forces, the procedure must be modified in the case of closed d -shell cations, to $\mathcal{E}^{(0)}(ab) = \alpha\omega E_1^{(0)}(ab)$. These attractive forces arise (in second order) because the excited cation states lie relatively low compared to those of ions which are isoelectronic with rare-gas atoms.

To a lesser degree the same effect must, however, be expected also in the heavy ions which are isoelectronic with rare-gas atoms if the interionic distance is small. It was observed in I that in the case of lithium iodide it is necessary to decrease the iodine-iodine repulsion as determined on the basis of $E_{\text{rep}}^{(0)}(ab) = \alpha E_1^{(0)}(ab)$ by

10%, implying $\omega = 0.9$ in the new notation, to stabilize this salt in the $B1$ configuration.

As in I, the good agreement between theoretical and experimental values for polymorphism and the deviations from the Cauchy relations suggests that the principal contributions to these deviations arise from three-ion short-range exchange forces. Further conclusions can be drawn on the basis of the present model with regard to the elastic constants of other compounds. For example, in solid MgO the electrostatic compression is higher, i.e., more shells of ions are in the repulsive field of a central ion. Such shells give a negative contribution to $c_{13} - c_{44}$ and we expect, accordingly, that $c_{13} - c_{44}$ for MgO will be more negative than for alkali halides. This is verified by experiment¹²: $c_{13} - c_{44}$ for MgO is -7.11×10^{11} dyn/cm² at 80°K, i.e., considerably more negative than the lowest value for alkali halides.

¹² M. A. Durand, Phys. Rev. **59**, 449 (1936).

R E S U M E

Le but de cette thèse est de montrer l'influence des interactions d'échange à trois ions sur la stabilité relative et sur les relations de Cauchy entre les constantes élastiques pour des cristaux ioniques simples (halogénures alcalins et cristaux ioniques dont les cations ont une couche complète d'électrons d).

L'analyse est basée sur le modèle de Born-Mayer auquel nous ajoutons des interactions non-Coulombiennes du type d'échange entre trois ions. L'énergie statique du réseau est exprimée comme somme de termes Coulombiens (énergie de Madelung) et non-Coulombiens. La partie de l'énergie provenant de l'interaction simultanée entre trois ions est déterminée relativement à la somme des énergies des trois paires séparées pour chaque configuration triangulaire possible dans le solide. Ces quantités relatives sont calculées en premier et deuxième ordres de théorie de perturbation en remplaçant la distribution électronique de chaque ion à couches complètes par un électron effectif avec distribution de charge gaussienne.

Les forces relatives entre trois ions suivent des lois très simples dépendant de la géométrie des triangles formés par ces trois ions. La contribution de l'interaction à trois ions à l'énergie statique du réseau est de l'ordre de quelques pourcent. Les déviations des relations de Cauchy sont calculées en sommant sur des contributions provenant d'interactions simultanées d'un ion central et de deux ions d'une même couche autour de ce ion.

Les résultats de cette analyse sont en accord avec les données expérimentales, d'une part pour la stabilité relative des quatre structures considérées (B1(NaCl), B2(CsCl), B3(ZnS) et B4(ZnO)), et d'autre part pour les déviations mesurées à basse température des relations de Cauchy $c_{13} = c_{44}$ et $c_{11} = 3c_{12}$ entre les constantes élastiques de cristaux de symétrie cubique ou hexagonale.

